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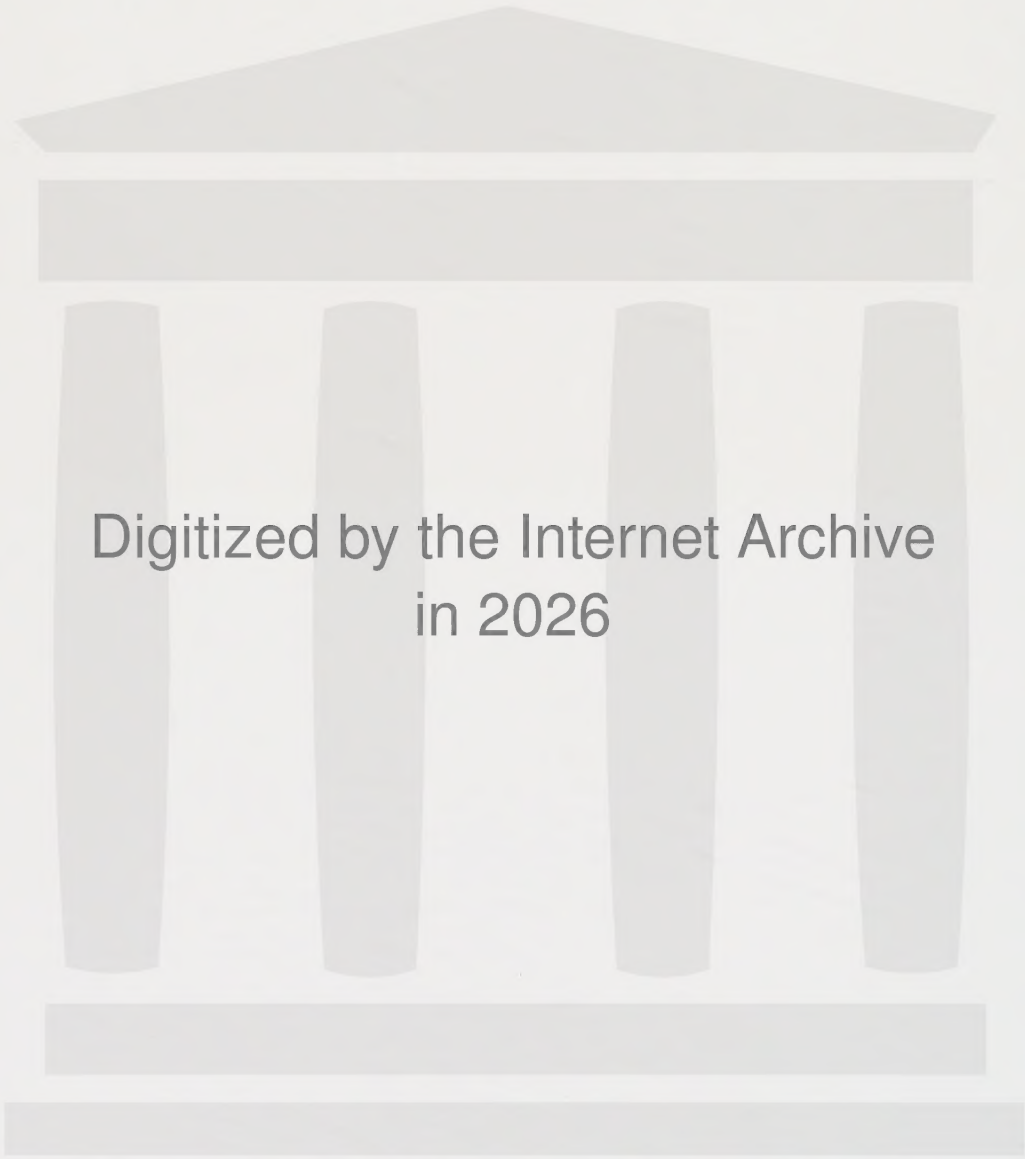
# IONIC EQUILIBRIA INVOLVING SOME OF THE MAJOR CONSTITUENTS OF SEAWATER

BY

BENGT ELGQUIST

GÖTEBORG 1978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# IONIC EQUILIBRIA INVOLVING SOME OF THE MAJOR CONSTITUENTS OF SEAWATER

BY

BENGT ELGQUIST

AKADEMISK AVHANDLING

för filosofie doktorsexamen (examinator professor David Dyrssen), som enligt kemisektionens beslut kommer att offentligt försvaras fredagen den 19 maj 1978 kl 1015 i föreläsningssal KD, kemihuset, Chalmers Tekniska Högskola, Göteborg.

GÖTEBORG 1978

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This thesis summarizes the contents of the following papers:

I. Determination of the stability constants of $MgF^+$ and $CaF^+$ using a fluoride ion selective electrode.
Bengt Elgquist, J. inorg. nucl. Chem., 1970, 32:937-944.

II. Sulphate complexation in seawater. A relation between the stability constants of sodium sulphate and magnesium sulphate in seawater from a determination of the stability of hydrogen sulphate and a calculation of the single ion activity coefficient of sulphate.
Bengt Elgquist and Margareta Wedborg, Marine Chemistry, 1974, 2:1-15.

IIa. Sulphate complexation in seawater - a reply.
Bengt Elgquist and Margareta Wedborg, Marine Chemistry, 1975, 3:79-80.

III. Stability of ion pairs from gypsum solubility. Degree of ion pair formation between the major constituents of seawater.
Bengt Elgquist and Margareta Wedborg, Marine Chemistry, 1975, 3:215-225.

IV. Stability constants of $NaSO_4^-$, $MgSO_4$, $MgF^+$, $MgCl^+$ ion pairs at the ionic strength of seawater by potentiometry.
Bengt Elgquist and Margareta Wedborg, Marine Chemistry, in press.

V. Stability constants of $CaSO_4$ and $CaCl^+$ at the ionic strength of seawater by potentiometry.
Bengt Elgquist and Margareta Wedborg, manuscript submitted to Marine Chemistry.

VI. Dissociation of hydrogen sulphide in seawater and comparison of pH scales.
Tom Almgren, David Dyrssen, Bengt Elgquist and Olof Johansson, Marine Chemistry, 1976, 4:289-297.

VII. Seawater neutralization of effluents from phosphorite consuming plants. A case study in the practical use of basic knowledge in analytical and marine chemistry.
David Dyrssen and Bengt Elgquist, manuscript submitted to Analytica Chimica Acta.

CONTENTS

Introduction

Activity and pH scales

Experimental methods

- Potentiometric measurements
- Spectrophotometric measurements
- Solubility measurements
- Problems concerning medium composition

Calculations

Results

Application of modified Gran plots to alkalinity measurements in anoxic seawater

Use of HALTAFALL for a practical case-study

Acknowledgements

References

# I N T R O D U C T I O N

Interactions among the constituents of seawater play an important role in marine biological and geochemical processes as well as analytical procedures for seawater. This thesis summarizes seven papers dealing with interactions among some of the major constituents of seawater ($Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $F^-$, $Cl^-$, $SO_4^{2-}$, $HCO_3^-$, and in anoxic waters $HS^-$).

Two approaches have been used to explain interactions among ionic species in electrolyte solutions when complex formation alone cannot explain experimental observations. The Debye-Hückel theory cannot predict all variations in activity in electrolyte solutions not even in solutions with ionic strength $< 0.1$ M. Many attempts have been made to modify the theory (e.g. Davies' formula). The first approach, the activity coefficient model for seawater (e.g. the models proposed by Whitfield[1,2], 1973, 1975) explains the interactions in terms of total activity coefficients and interaction coefficients. The second approach, the ion pair formation model, describes the interactions in terms of ion pair formation between cations and anions (however, even polynuclear species like $MgCaCO_3^{2+}$ and $Mg_2CO_3^{2+}$ have been proposed by Hawley[3]). Due to strong ion-dipole bonds, hydrated metal ions have a tendency to form outer-sphere complexes, but probably other factors than electrostatic attraction (e.g. entropy changes upon ion pair formation)

must be taken into consideration when relations between ion pair stabilities are to be explained. The physical existence of ion pairs cannot be proved with the experimental techniques used in this work. Raman spectroscopy, however, provides evidence for the existence of $NaSO_4^-(H_2O)_x$ and $MgSO_4(H_2O)_x$ (Daly et. al.[4]). Eigen and Tamm[5] (1962) and Fischer[6] (1967) assume the existence of the ion pair $MgSO_4$ to explain ultrasonic absorption data.

At the present state neither of the two approaches can satisfactorily explain all experimental data from measurements of ionic interactions in seawater. For two important reasons the ion pair formation approach is used in this work. The first is that it facilitates vizualization of the processes. The second reason is the existence of the very general and powerful computer program HALTAFALL (Ingri et. al.[7], 1967). "HALT" is a Swedish word for concentration, "FALL" means formation of solid phase (or phases). From stability and distribution constants, solubility products and total concentration data, the program computes the concentrations at equilibrium of all species in the solution using a generalized form of mass balance equations. Problems including two liquid phases, gas phase, solid phases, titration procedures and redox equilibria can easily be solved provided that adequate equilibrium constants are available (for problems concerning gas equilibria and solid phases the program SOLGASMIX constructed by Eriksson[8] (1975) is

perhaps more suitable). Furthermore, titration procedures can be calculated and titration curves predicted even if the procedure includes extremely complex equilibria. As a consequence, the uncovering of systematic errors within analytical titration procedures is very much facilitated, provided that equilibrium is reached in all titration points. (E.g. see Jagner[9], 1971, and Anfält[10], 1972). The two approaches are further discussed in papers II, IIa, IV and V.

An attemp to calculate the concentrations of the main dissolved species of the major elements (as well as the minor and micro elements) of seawater was made by Sillén[11] (1961). Garrels and Thompson[12](1962) calculated the distribution of the major constituents of seawater from stability constants valid for zero ionic strength and activity coefficients valid for the ionic strength of seawater. At that time very few (if any) stability constants for the ion pairs formed by the major constituents, and determined at the ionic strength of seawater, were available. Dyrssen and Wedborg[13](1973) used HALTAFALL to calculate the speciation of the elements in seawater. A recalculation of the distribution of the major constituents (and borate) of seawater, based on constants from Dyrssen and Hansson[14](1972) and this work, is given in paper III. In this calculation the ion pairs $MgCl^+$ and $CaCl^+$ are taken into consideration.

## A C T I V I T Y  A N D  p H  S C A L E S

Usually the activity scale is defined so that

$$a_x = f_x[X] \; ; \quad f_x \rightarrow 1 \text{ when } [X] \rightarrow 0 \text{ in pure water}$$

where $a_x$ is the activity of ion X and

$f_x$ is the free ion activity coefficient of X.

Since seawater is a solution of moderately high ionic strength this scale is not particularly suitable for marine chemistry and biology. Sillén[15](1967) proposed another scale for minor species in seawater.

$f_x \rightarrow 1$ when $[X] \rightarrow 0$ in 0.7 M NaCl or 35 o/oo seawater.

In paper I the activity scale for $F^-$ is defined so that

$f_{F^-} \rightarrow 1$ when $[F^-] \rightarrow 0$ at the constant formal ionic strength used (0.1-1.0 M).

In papers IV and V the following assumption is made: the free single ion activity coefficients depend only on the formal ionic strength, i.e. the stability of an ion pair is independent of medium composition at constant formal ionic strength. This assumption is of course an approximation. In paper V it is shown that the stability of the ion pair $CaSO_4$ is slightly medium dependent. Thus it is desirable to minimize alterations in medium composition; on the other hand the medium alterations must be large enough to yield a measurable EMF (absorbance, solubility) change. Thus, the design of the experimental procedure is a compromise.

The method usually adopted for determination of pH in seawater is based on calibration with NBS buffer solutions. Hansson[16](1973) pointed out that this method neither gives concentration of $H^+$ nor activity of $H^+$ on any activity scale but merely a value on the pH-meter. He suggested a new pH scale for seawater based on an activity scale defined so that

$$f_{H^+} \rightarrow 1 \text{ when } [H^+] \rightarrow 0 \text{ in pure synthetic seawater}$$

and a set of standard buffers composed of "tris" (2-amino--2-hydroxymethylpropane-1,3-diol), "tris" hydrochloride and synthetic seawater. In paper VI it is pointed out that determinations of the stability of $H_2S$ in synthetic seawater and sodium chloride solutions can be used to compare the pH scales suggested by Hansson and by Bates[17] (1975) and to compare the conventional pH scale with Hansson's titration pH scale. At the Dahlem workshop on "The Nature of Sea Water" (1975) Hansson et.al.[18] recommended a new scale based on the relationship

$$p\, m_H = -\log(m_H)_X$$

where $m_H$ is the molality of free hydrogen in a seawater sample X. The relation between this new scale and Hansson's titration scale is further discussed by Almgren[19](1975), Bates and Culberson[20](1977), and in paper VI.

# E X P E R I M E N T A L  M E T H O D S

A wide variety of experimental techniques have been employed for determination of ion pairing. However, from an analytical point of view and taking into account the high ionic strength of seawater, potentiometry, spectrophotometry and solubility measurements are considered the most appropriate methods. Determination of equilibrium constants requires a considerable number of measurements in order to minimize the experimental uncertainty. This applies especially to the determination of weak complexes like ion pairs. When potentiometry or spectrophotometry is applied, titration procedures offer some advantages over single point measurements, e.g., the greater amount of experimental data obtained in an experiment. A desirable condition for the use of titration procedures is rapid reaction kinetics. The equilibria studied in this work appear to be practically instantaneous. Potentiometric titrations are applied in papers I and IV-VII and spectrophotometric titrations in paper II.

## Potentiometric measurements

Potentiometry offers the possibility of following the free ion activity during a titration. Some factors which influence the suitability of an electrode used for determination of stability constants should be mentioned. The stability of the electrode potential often depends on

the electric resistance of the electrode. A low resistance favours good stability. The Nernstian slope

$$Z = \frac{RT\ln 10}{nF}$$

should be close to the theoretical value. A value deviating from the theoretical one indicates an incomplete electrode reaction, e.g. as an result of interference from other ions in the solution.

The solid state ($LaF_3$) fluoride electrode is probably the best of the many new electrodes which have appeared during the last ten years. It is stable, reliable, has few interferences and the Nernstian response is close to the theoretical value. Lanthanum ions interfere but do not appear in the solutions used in this work. $OH^-$ interferes probably because $F^-$ and $OH^-$ are isoelectronic, have equal charges and have similar ionic radii. The fluoride electrode is used to determine the stability of $MgF^+$ and $CaF^+$ (paper I) and the stability of $MgSO_4$ and $MgCl^+$ indirectly (paper IV). This indirect determination could be explained in terms of conditional constants (Ringbom[21], 1963); The conditional stability constant of $MgF^+$ is determined in different media of equal formal ionic strength. The differences in stability among different media are used to calculate the stability constants of $MgSO_4$ and $MgCl^+$.

A cell with a sodium sensitive glass electrode and a

solid state chloride electrode was used for the determination of the stability constant of $NaSO_4^-$ (paper IV). Since the total chloride concentration was kept constant during the titrations, the chloride electrode can be regarded as a reference without liquid junction. The absence of liquid junction potential is considered an advantage as the interaction between sodium and sulphate is rather weak. Since $[H^+]$ is 5 to 6 orders of magnitudes lower than $[Na^+]$, slight variations in $[H^+]$ does not influence the EMF of the cell.

For the determination of the relationship between the stabilities of $CaSO_4$ and $CaCl^+$, an improved calcium electrode with a PVC matrix membrane was used (paper V). The calcium electrode is not as suitable for stability determinations as the sodium and fluoride electrodes. However, at the present time it is perhaps the best available considering e.g. the improved selectivity for $Ca^{2+}$ over $H^+$ and $Na^+$. Finally, a glass electrode is used to follow pH when a solution containing fluoride and silicon fluorides from the effluents of a superphosphate processing plant is titrated with seawater (paper VII). The potentiometric titrations of papers IV and V are performed by means of a semi-automatic computer system described in paper IV.

Spectrophotometric measurements

The uncharged base diphenylamine has a high molar

absorptivity at 278 nm and a protonization constant

$$K_{HB^+} = \frac{[HB^+]}{[H^+][B]} \qquad B = \text{diphenylamine}$$

in the same range as the stability constant of $HSO_4^-$ (paper II). Once $K_{HB^+}$ is determined, $[H^+]$ can be measured indirectly. This method is used in paper II to determine the conditional stability of $HSO_4^-$ in two different media of 0.7 M formal ionic strength. Because of the high molar absorptivity, the concentration of diphenylamine can be kept as low as 10 uM. Consequently diphenylamine can be excluded from the mass balance equations and this of course facilitates the calculations.

Solubility measurements

Although solubility measurements have the drawback of yielding only one experimental value per experiment, the data produced (total concentrations) are well defined. Paper III deals with measurements of the solubility of $CaSO_4.2H_2O$ (gypsum). For several reasons this salt is preferred to less soluble salts formed by the major constituents of seawater, e.g. $MgF_2$, $CaF_2$ and $CaCO_3$. The equilibria determining the solubility of $CaCO_3$ are pH dependent and buffer substances cannot be added. The solubilities of $MgF_2$ and $CaF_2$ are rather low and equilibrium is reached slowly (15-50 hours at 25°C). On the other hand, the solubility of gypsum has been widely studied, especially its solubility in brines from desalination plants, so comparisons can be made with

data from the literature. From gypsum solubility in 22 different media of 0.7 M formal ionic strength, the stability constants for $NaSO_4^-$, $KSO_4^-$, $CsSO_4^-$, $MgSO_4$, $CaSO_4$, $MgCl^+$ and $CaCl^+$ are calculated.

Problems concerning medium composition

As long as equilibrium concentrations of ion pairs cannot be measured directly, they have to be calculated from measurements of the concentration of one (or both) of the ions forming the ion pair. This complicates the problem of medium composition when constant formal ionic strength is used because other ions than those forming the ion pair always must be added. Since the determined stability constants are to be valid for seawater, the choice of medium ions is rather limited. It is necessary to make assumptions about the stability constants of some couples of ions, otherwise the results would just be relationships between the stabilities of ion pairs. If the formation of ion pairs is mainly due to electrostatic forces, Coulomb's law favours ion pair formation between ions of high electrostatic charge per ion radius. In fig. 1 log K for some ion pairs are plotted versus $z_+z_-$. It is reasonable to assume that ion pairs formed by unity charged ions do exist but that they are very weak. For example, Miller[22](1974) found a value of 0.05 for $K_{NaF}$ in sodium chloride (I=0.7M) but he did not take NaCl ion pair formation into account. In the present work ion pair formation between ions of unity charge is neglected.

Perchlorate is often used as a reference ion for anions since it is asumed to be free from interactions with the cations present. However, perchlorate is not a constituent of seawater. Furthermore, perchlorate cannot be used in systems containing a calomel electrode ($KClO_4$ precipitates) or a calcium electrode of the type used in this work (serious interference). Nevertheless perchlorate is used in this work when possible since no better alternative is available.

Since this is a work in analytical and marine chemistry molar units are preferred to molal units used in physical chemistry. However, it is believed that in future work weight molar units (denoted $M_w$, number of moles of solute per 1000 g. solution) is a good alternative since concentrations expressed on this scale are independent of temperature and pressure and weighing offers greater precision than volume measuring.

## C A L C U L A T I O N S

The problem of calculating stability constants from experimental data can be solved in many ways. However, when the experimental data originates from titration procedures, minimization of an error square sum

$$U = \sum^{n} (E_{obs} - E_{calc})^2$$

where n is the number of experimental points

$E_{obs}$ is the observed value (EMF etc.)

$E_{calc}$ is a calculated value

is an advantageous method. It takes all points into consideration; there is no need for approximations; it is well suited for computerization and it gives a quantitative value of the discrepancy between calculated and observed titration curves. The theoretical base for least square sum calculations is given by Dyrssen et. al.[23] (1961) and Sillén[24] (1962). Sillén et.al. (e.g. see Sillén and Warnqvist[25]) also constructed the generalized computer program LETAGROP (LETA is Swedish for search, GROP means pit, i.e. the minimum of the n-dimensional error square sum function). The method of minimization of error square sums is used throughout this work. The calculations were performed in double numerical precision by means of computer programs written in BASIC mainly on an IBM 360/65 computer.

## R E S U L T S

The stability constants determined in this work are summarized in Table 1.

In papers IIa, III and IV it is pointed out that the results of stability constant determinations often vary with the experimental method used which is analogous to the fact that results from chemical analysis often vary with the method used. The conclusion is that variations in results from different methods of determining stability constants supersede the experimental error of any particular method. One possible and plausible explanation is that one measures somewhat different effects with different methods.

## Application of modified Gran plots to alkalinity measurements in anoxic seawater

The methods of evaluating equivalence points proposed by Gran[26] (1952) have become almost standard in connection with potentiometric titrations during the last ten years. Hansson and Jagner[27] (1973) outlined a Gran procedure for the potentiometric determination of total alkalinity in seawater. If this method is applied to alkalinity determinations in anoxic seawater, the Gran plot is modified with regard to formation of $H_2S$ from $HS^-$. In paper VI the stability constants for $H_2S$ in seawater (2.5 - 40 o/oo salinity) and sodium chloride solutions at 5° and 25°C are given.

## Use of HALTAFALL for a practical case study

Paper VII gives an example of the power of the HALTAFALL program for calculating the concentration of each species during the dilution and neutralization of effluents from a superphosphate processing plant with seawater. The problem includes rather complicated equilibria and the calculation exemplifies the use of a nonexisting component (in this case $Si^{4+}$) together with an arbitrary scale for stability constants and simulation of equilibrium between solution and a gas phase. The stability constants for $MgF^+$ and $CaF^+$ from paper I were used for the HALTAFALL calculation. The calculations were checked by a potentiometric titration with glass and fluoride electrodes.

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References

1. Whitfield,M., 1973. A chemical model for the major electrolyte components of seawater based on the Brønsted - Guggenheim hypothesis. Mar. Chem., 1 : 251-266.

2. Whitfield, M., 1975. An improved specific interaction model for seawater at 25°C and 1 atmosphere total pressure. Mar. Chem., 3 : 197-213.

3. Hawley, J.E., 1973. Bicarbonate and carbonate ion association with sodium, magnesium and calcium at 25°C and 0.72 ionic strength. Thesis, Oregon State University.

4. Daly, F.P., Brown, C.W. and Kester, D.R., 1972. Sodium and magnesium sulfate ion pairing: Evidence from Raman Spectroscopy. J. Phys. Chem., 76 : 3664-3668.

5. Eigen, M. and Tamm, K., 1962. Sound absorption in electrolytes as a consequence of chemical relaxation. Z. Elektrochem., 66 : 107-121.

6. Fischer, F.H., 1967. Ion pairing of magnesium sulfate in seawater: Determined by ultrasonic absorption. Science, 157 : 823.

7. Ingri, N., Kakolowicz, W., Sillén, L.G. and Warnqvist, B., 1967. High-speed computers as a supplement to graphical methods - V. Talanta, 14 : 1261-1286. Errata: Talanta (1968), 15 : xi.

8. Eriksson, G., 1975. SOLGASMIX, a computer program for calculation of equilibrium compositions in multiphase systems. Chem. Scr., 8 : 100-103

9. Jagner, D., 1971. A computer treatment of theoretical and practical aspects of titration procedures. With special reference to the development of automatic high precision methods for the determination of some of the major constituents of seawater. Thesis, University of Gothenburg.

10. Anfält, T., 1972. An investigation of some ion-selective electrodes for use in automatic titrations. Thesis, University of Gothenburg.

11. Sillén, L.G., 1961. The physical chemistry of seawater. In Oceanography. Amer. Assoc. Adv. Sci., Washington, D.C., pp. 549-582.

12. Garrels, R.M. and Thompson, M.E., 1962. Chemical model for seawater at 25°C and 1 atmosphere total pressure. Am. J. Sci., 260 : 57-66.

13. Dyrssen, D. and Wedborg, M., 1973. In: Goldberg, E.D. (Editor), The Sea, vol 5. Equilibrium calculations of the speciation of elements in seawater. John Wiley & Sons Inc.

14. Dyrssen, D. and Hansson, I., 1972. Ionic medium effects in seawater. A comparison of the acidity constants of carbonic acid and boric acid in sodium chloride and synthetic seawater. Mar. Chem., 1 : 137-149.

15. Sillén, L.G., 1967. Master variables and activity scales. In: Equilibrium Concepts in Natural Water Systems, Adv. in Chem. Ser. 67, Amer. Chem. Soc., Washington, D.C.

16. Hansson, I., 1973. A new set of pH-scales and standard buffers for seawater. Deep-Sea Res., 20 : 479-491.

17. Bates, R.G., 1975. pH-scales for seawater. In: Goldberg, E.D. (Editor). The Nature of Sea Water, paper 10. Pergamon Press, Oxford.

18. Hansson, I., Ahrland, S., Bates, R.G., Biedermann, G., Dyrssen, D., Högfeldt, E., Martell, A.E., Morgan, J.J., Schindler, P.W., Warner, T.B. and Whitfield, M., 1975. Conventions for seawater equilibria. Group Report. In: Goldber, E.D. (Editor). The Nature of Sea Water. Dahlem Konferenzen, Berlin.

19. Almgren, T., 1975. Advances in Analytical Methods for the Study of some Seawater Constituents. Thesis, University of Gothenburg.

20. Bates, R.G. and Culberson, H., 1977. Hydrogen ions and the thermodynamic state of marine systems. In: Andersen, N.R. and Malahoff, A. (Editors). The fate of fossil fuel $CO_2$ in the oceans. Plenum Press, pp. 45-61.

21. Ringbom, A., 1963. Complexation in analytical chemistry. In: Chemical Analysis, XVI. Interscience, New York, N.Y. and London.

22. Miller, G.R., 1974. Fluoride in seawater. Thesis, **University of Rhode Island.**

23. Dyrssen, D., Ingri, N. and Sillén, L.G., 1961. "Pit-mapping - a general approach for computer refining of equilibrium constants. Acta Chem. Scand., 15 : 694-696.

24. Sillén, L.G., 1963. High-speed computers as a supplement to graphical methods. 1. Functional behaviour of the error square sum. Acta Chem. Scand., 16 : 159-172.

25. Sillén, L.G. and Warnqvist, B., 1969. High-speed computers as a supplement to graphical methods. 6. A strategy for two--level LETAGROP adjustment of common and "group" parameters. Some features that avoid divergence. Arkiv Kemi, 31 : 315-339.

26. Gran, G., 1952. Determination of the equivalence point in potentiometric titrations, part II. Analyst, 77 : 661-671.

27. Hansson, I. and Jagner, D., 1973. Evaluation of the accuracy of Gran plots by means of computer calculations. Application to the potentiometric titration of the total alkalinity and carbonate content in seawater. Anal. Chim. Acta, 65 : 363-373.

Table 1. Stability constants determined (paper I-VI). 25°C an 1 atm. total pressure if not otherwise stated. PT = potentiometric titrations, SpT = spectrophotometric titrations, Sol = solubility of gypsum, I = ionic strength (formal), SSW = synthetic seawater.

| Species | Method | Medium | Stability constant | Ref. | Remark |
|---|---|---|---|---|---|
| $HSO_4^-$ | SpT | I = 0.7 M | $17.0 \pm 0.1$ | II | cond. constant |
| " | | " | $\sim 30$ | III | calculated |
| $NaSO_4^-$ | Sol | " | 1.22 | " | |
| " | PT | " | $1.8 \pm 0.1$ | IV | |
| $KSO_4^-$ | Sol | " | 1.84 | III | |
| $CsSO_4^-$ | " | " | 2.45 | " | |
| $MgSO_4$ | " | " | 12.3 | " | |
| " | PT | " | 6.3 | IV | |
| " | | " | $\sim 6.4$ | II | calculated, $K_{NaSO_4} = 1.8$ |
| $CaSO_4$ | Sol | " | 30.6 | III | |
| " | PT | " | $17.7K_{CaCl} + 16.5$ | V | $K_{NaSO_4} = 1.8$ ; $0 \leq K_{CaCl} \leq 1$ |
| " | " | " | $18.8K_{CaCl} + 17.3$ | " | $K_{NaSO_4} = 2.0$ ; $0 \leq K_{CaCl} \leq 1$ |
| $MgF^+$ | " | I = 0.1 M | $28.7 \pm 1.7$ | I | cond. const. = $\frac{K_{MgF}}{1 + K_{MgCl}[Cl^-]}$ |
| " | " | I = 0.4 M | $22.0 \pm 1.6$ | " | |

Table 1 (cont.)

| Species | Method | Medium | Stability constant | Ref. | Remark |
|---|---|---|---|---|---|
| $MgF^+$ | PT | I = 0.7 M | 18.8 ± 0.7 | I | cond.const. = $\frac{K_{MgF}}{1 + K_{MgCl}[Cl^-]}$ |
| " | " | I = 1.0 M | 18.6 ± 0.8 | " | " |
| " | " | I = 0.7 M | 18.5 | IV | " calc., $K_{MgCl} = 0.34$ |
| " | " | " | 22.9 ± 0.1 | " | |
| $CaF^+$ | " | I = 0.4 M | 5.01 ± 0.16 | " | cond. const. = $\frac{K_{CaF}}{1 + K_{CaCl}[Cl^-]}$ |
| " | " | I = 0.7 M | 4.22 ± 0.07 | " | " |
| " | " | I = 1.0 M | 3.85 ± 0.08 | " | " |
| $MgCl^+$ | Sol | I = 0.7 M | 0.48 | III | |
| " | PT | " | 0.34 ± 0.02 | IV | |
| $CaCl^+$ | Sol | " | 1.20 | III | |
| " | PT | " | | V | relation with $K_{CaSO_4}$ |
| $H_2S$ | " | SSW 5°C, 5-40o/oo | log K 7.10-6.98 | VI | cond. constant |
| " | " | SSW 2.5-40 o/oo | log K 6.81-6.58 | " | " |
| " | " | 0.1 $M_w$ NaCl 5°C | log K 7.14 | " | |
| " | " | 0.7 $M_w$ NaCl 5°C | log K 7.08 | " | |
| " | " | 0.1-0.8 $M_w$ NaCl | log K 6.79-6.72 | " | |

Table 1 (cont.)

| Species | Method | Medium | Stability constant | Ref. | Remark |
|---|---|---|---|---|---|
| $H_2S$ | PT | 0.35 M NaCl<br>0.12 M $CaCl_2$ | log K 6.71 | VI | cond. constant |
| $HB^+$ | SpT | I = 0.7 M | log K 0.89 $\pm$ 0.01 | II | B = diphenylamine |
| $MgHSO_4^+$ | | " | $\sim$ 3.9 | III | calculated, $K = \frac{[MgHSO_4^+]}{[Mg^{2+}][HSO_4^-]}$ |
| $CaSO_4.2H_2O$ Sol | | " | $K_{so}$ $2.87.10^{-4}$ | " | |

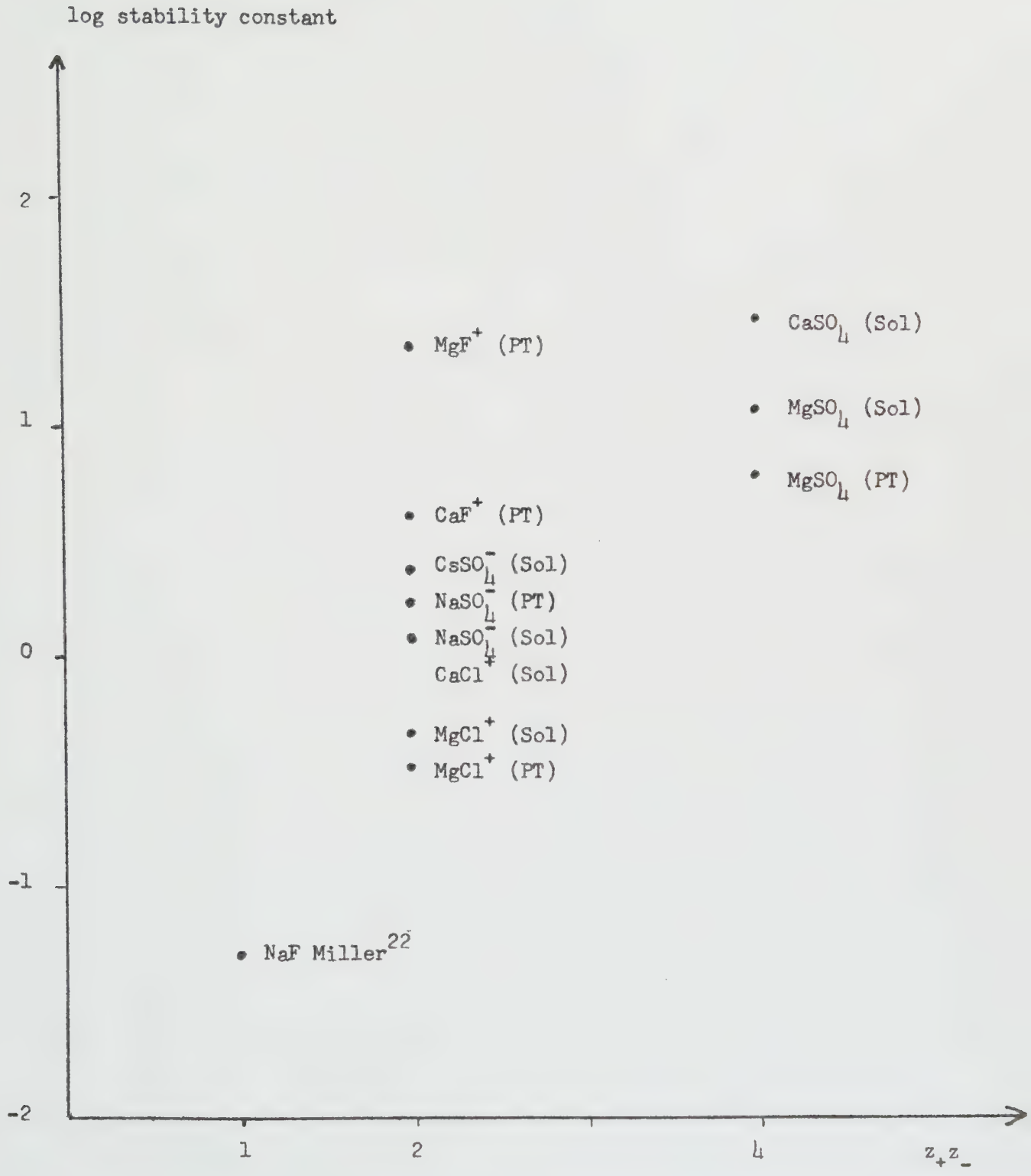


Fig. 1. Logarithms of stability constants for some ion pairs versus the product of the charges of the ions forming the ion pair. 25°C and 0.7 M formal ionic strength.